Thermodynamics of Coal Chars; Correlation of Heat
Capacity with Composition and Pyrolysis Conditions

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Introduction

Heat capacity data for a char can be used to calculate the
variation of the thermodynamic properties, H, S, G, etc. with
temperature. Factors which affect the heat capacity are:

o   the rank and inorganic matter content of the parent coal;
o   the gaseous atmosphere present during pyrolysis;
o   the thermal history of the char.

Thermal history for a char is determined by:

o   the pyrolysis temperature;
o   the rate at which the coal temperature is raised from
    the ambient to the pyrolysis temperature;
o   the residence time of the char at the pyrolysis
    temperature.

The thermodynamic literature (1-5) for chars usually covers
only limited temperature ranges and the thermal histories and
compositions of the char samples are ill-defined or unavailable.
The additivity approach (6,7) is usually employed to correlate
the heat capacities in terms of char constituents; organic matter,
ash and moisture.

In the thesis work of Wang (8) the effect and relative impor-
tance of the factors listed was assessed using a selected set of
chars. Experimental data was collected between $80^{\circ}K$ and $300^{\circ}K$.
It was found that the heat capacities could be correlated with
compositions and pyrolysis temperatures using a modified form of
the Debye model for heat capacities (9). The correlation is in
the form of an expression for an effective Debye temperature, $\theta(Tr)$:

$$\theta(Tr) = \theta_{o}(Tr) \exp[I(Tr)/x(1-x)] \qquad\qquad 1)$$

where Tr is a reduced temperature defined as:
$$Tr = T(K)/T_{pyrolysis} \quad (K)$$

1-x =   the atomic fraction of carbon in the ash
        free dry char.

$\theta_o(Tr)$ = a Debye temperature at Tr for a hypothetical char containing carbon atoms only.

$I(Tr)$ = an interaction parameter between the carbon atoms and the "other" atoms in the char.

θ_o and I were found by empirical fitting of the data for each family of chars. A char family consists of all the chars prepared from the same coal with one hour residence time.

Our present objective is to:

o Test the limits of applicability of Equation 1 as an extrapolating function to calculate heat capacities of chars;
o To refine the correlation model;
o To factor into the correlating the effect of residence time at pyrolysis temperature.

Experimental Technique

The suite of samples from Wang's work was used for heat capacity measurements between $300^{o}K$ and $900^{o}K$. The data were obtained using the differential scanning calorimetry (DSC) technique. Instrumentation consisted of a Dupont model 910 scanning calorimeter and a Dupont model 1090 thermal analyzer system. Sample heat capacities were calculated using the measured heat capacity of Sapphire as a standard for comparison.

Results

Typical experimental information obtained is illustrated in the following figures.

Effect of Pyrolysis Temperature

In Figure 1 we show DSC scans for two chars prepared from demineralized Virginia Coal (PSOC-265). The results show that the heat capacity of the chars increase with temperature between 300K and 900K. Also the char prepared at $1100^{o}C$ has a higher heat capacity at any given temperature (over the range) than the $700^{o}C$ char. For quantitative comparison the heat capacities need to be normalized. The normalizing procedure is arbitrary. We have elected to normalize all our data to the number of atoms in the ash free char.

Effect of Residence Time

In Figure 2 we show DSC scans for chars prepared from demineralized Virginia coal at $1100^{o}C$ pyrolysis temperature.

The chars differ in their thermal history by the length of their residence time at pyrolysis temperature. The normalized heat capacities at a given temperature vary in magnitude with the residence time.

A minimum in heat capacity is seen to occur if the data is replotted as heat capacity versus residence time. From the present data the minimum is around two hours residence time. Our interpretation of this phenomenon is that two separate events are being observed. One is the equilibration of the chemical composition at $1100^{\circ}C$ by breakage of C-H bonds. The smaller the number of such bonds in the char the smaller is its heat capacity. The second is the approach of the char to structural equilibrium by solid state diffusion. The char is graphitizing with an apparent increase in heat capacity.

Effect of Retained Inorganic Matter

In Figure 3 the DSC scans of chars prepared at $700^{\circ}C$ with one hour residence time are compared. Both of these chars were prepared from Virginia coal. However, in one case the coal was demineralized using the acid wash procedure prior to pyrolysis. On a per gram sample basis the heat capacity of the mineral matter containing char is about 40 to 80% higher than the demineralized char. The inorganic matter heat capacity is additive to the organic matter heat capacity.

Conclusions

At the time of preparation of this preliminary paper (December 1982) the calculation for testing and refining the correlation model have not been completed. We expect to be able to present them at the meeting.

References

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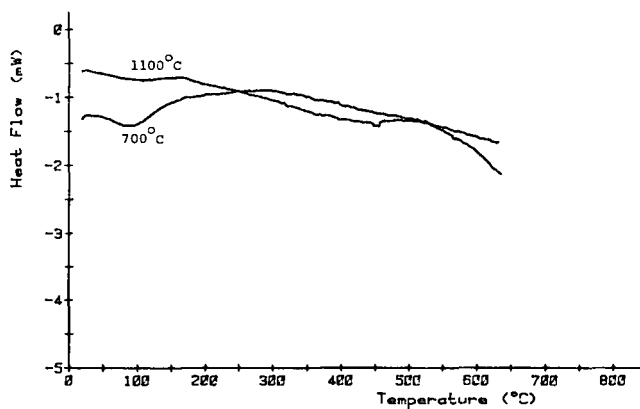9. Maradudin, A.A. in "Solid State Physics"(Academic Press, 1966) 18: p. 274.

Figure 1. DSC Scans on Virginia Chars. (One hr. residence
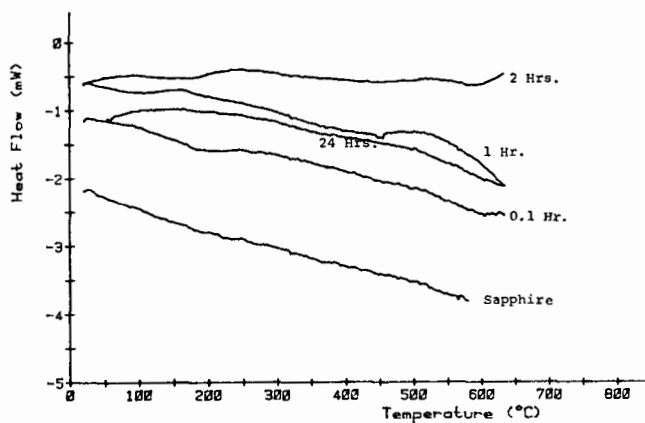time - demineralized).

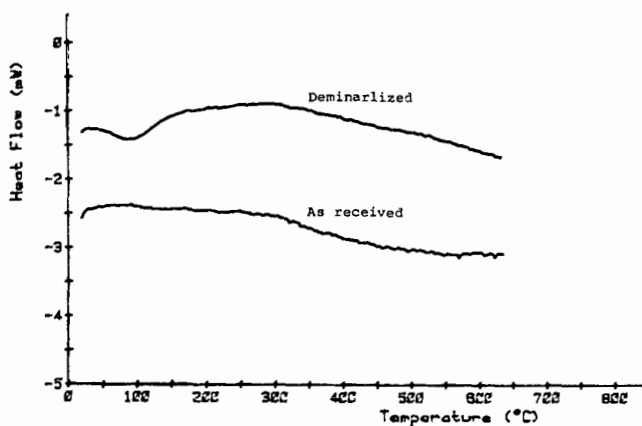Figure 2. DSC Scans on Virginia chars. (1100°C Demineralized)

Figure 3. DSC Scans on Virginia chars. (700°C - One hour residence time)

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